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Systems Analysis of Ionic Liquids for Post-combustion CO_2 Capture at Coal-fired Power Plants

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Abstract

The main objective of this study is to investigate the feasibility and costs of ionic liquid (IL)-based CO_2 capture systems at pulverized coal-fired (PC) power plants. The IL selected for this assessment is trihexyl-(tetradecyl)phosphonium 2-cyanopyrrolide ([P66614][2-CNpyr]), achieving a 1:1 and reversible chemical reaction between $[2\text{-CNpyr}]^-$ and CO_2. A multi-stage equilibrium-based modeling framework is established to simulate the adiabatic absorption process, whereas a single-stage flash drum in equilibrium is employed for the stripping process. The performance model is linked to an engineering-economic model that estimates the capital cost, annual operating and maintenance (O&M) costs, and total levelized annual cost. The technical and cost models are applied to estimate the cost of CO_2 captured by an IL-based CCS system. The preliminary results show that for 90% CO_2 capture, the capture cost would be higher than the U.S. Department of Energy's target at $40 per metric ton of CO_2 captured for new generation technologies, mainly due to a large capital cost. However, current process designs are not yet optimized. Based on the cost of CO_2 captured, the most cost-effective capture cost is found to be at a removal efficiency of about 85% for CO_2.

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Keywords: Systems analysis; post-combustion CO_2 capture; ionic liquids

1. Introduction and Research Objective

Ionic liquids (ILs) are among the new materials being developed for carbon dioxide (CO_2) capture because of their many favorable properties: nonvolatile, high thermal stability, high CO_2 solubility and selectivity, and endless

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tenability. Both chemical and physical properties of ILs may be "tailored" by varying their structure or chemical constitution to improve the carrying capacity and decrease the energy penalty for CO_2 capture [1-2]. Current research on ILs is focused mainly on materials synthesis, laboratory experiments and molecular simulation of physical and chemical properties. However, few efforts have been made to analyze IL-based CO_2 capture processes. The main objective of this study, therefore, is to investigate the feasibility and costs of IL-based CO_2 capture systems at pulverized coal-fired power plants.

2. Performance Model for Ionic Liquid-based CO_2 Capture

The purpose of the performance model is to establish the mass flows and energy requirements needed to achieve a specified level of CO_2 capture and storage at a power plant with user-specified design and operating characteristics. This study employs the typical absorption and stripping process for IL-based carbon capture. Figure 1 shows a simple schematic of the process.

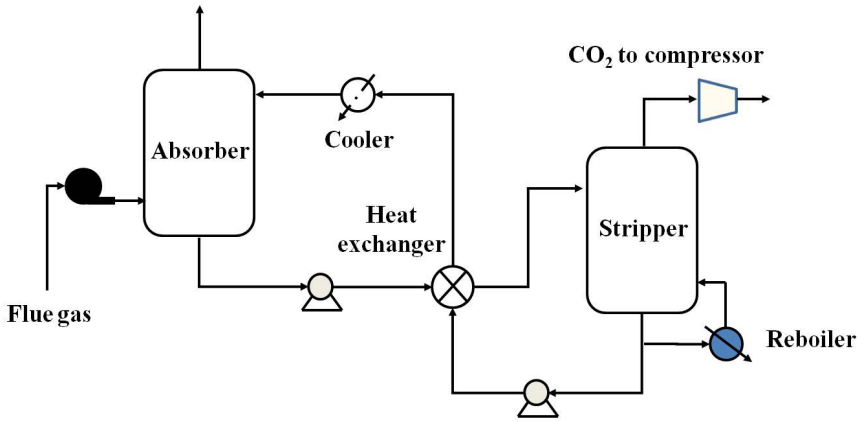

Fig. 1 A process schematic

Nomenclature

C_3:	measure of reaction site density	T:	temperature
d_p:	nominal packing diameter	V:	gas flow rate or molar volume
D:	diffusion coefficient	x:	mole fraction in liquid phase
E:	enhancement factor	X:	mole ratio in liquid phase
g:	gravity	y:	mole fraction in gas phase
h:	enthalpy of liquid flow	$\dot{a}$:	wetted packing area
H:	enthalpy of gas flow	$\dot{a_p}$:	total packing area
Hn:	Henry's law constant	σ_c:	critical surface tension of packing material
ΔH:	reaction heat	σ:	surface tension
k_1:	reaction equilibrium constant	μ:	viscosity
K:	phase equilibrium ratio	ρ:	density
k_G:	gas-phase mass transfer coefficient	∅:	fugacity coefficient
K_G:	overall gas-phase mass transfer coefficient		
k_L:	liquid-phase mass transfer coefficient	**Subscripts:**	
L:	solvent flow rate	i:	component
n:	number of moles	j:	stage number
m:	slope	G:	gas phase
P:	pressure	L:	liquid phase
Q:	cooling duty	V:	vapor phase
R:	gas constant		

In addition to the absorber and stripper, a variety of other equipment is installed to support the capture process. A

blower is used to offset the pressure drop of flue gas across the absorber. A direct contact cooler (DCC) is used to lower the temperature of flue gas into the absorber where an absorption intercool may be installed to remove the reaction heat. A solvent cooler also is used to lower the temperature of lean solvent into the absorber. A lean/rich solvent heat exchanger is designed based on a given cold-side temperature approach to recover heat from the hot lean solvent. The CO_2 product out of the stripper is compressed via a multi-stage compressor to the supercritical condition needed for transport and storage.

2.1. Development of a Multi-stage Equilibrium Model for Gas Absorption

Absorption of CO_2 using ILs is considered as a steady-state vapor-liquid process consisting of a number of stages. Equilibrium is assumed to take place between vapor and liquid streams leaving each stage. A multi-stage equilibrium model is established to simulate the absorption process. As discussed below, the multi-stage process model takes into account the mass balance (M), equilibrium (E), summation (S), and enthalpy balance (H). In this framework, a Langmuir absorption model that incorporates both the stoichiometric reaction and physical uptake is used to describe the equilibrium for the selected ILs for chemical absorption [1]. The Newton-Raphson simultaneous correction algorithm is applied to solve the MESH equations and then provide the profiles of vapor and liquid compositions and temperatures across all equilibrium stages.

***M**ass balance for each component at each stage (j)*:

$$L_{j-1}x_{i,j-1}-L_jx_{i,j}+V_{j+1}y_{i,j+1}-V_jy_{i,j}=0 \quad (1)$$

***E**quilibrium for each component at each stage (j)*:

For chemical absorption processes, a Langmuir-type absorption model that incorporates both the stoichiometric reaction and physical uptake is used to describe the equilibrium [1-2]. Total CO_2 uptake on the basis of mole ratio for absorbed CO_2 versus initial IL is predicted in terms of CO_2 partial pressure, Henry's law constant, and reaction equilibrium constant as [1]:

$$X_{co2,j}=\frac{n_{CO2}}{n_{IL_o}}=\frac{P_{CO2,j}/Hn_j}{1-P_{CO2,j}/Hn_j}+\frac{k_{1,j}P_{CO2,j}C_3}{1+k_{1,j}P_{CO2,j}} \quad (2)$$

***S**ummation based on mole fractions for each stage (j)*:

$$\sum y_{i,j}=1 \quad (3)$$

$$\sum x_{i,j}=1 \quad (4)$$

***E**nthalpy balance for each stage (j)*:

$$L_{j-1}h_{j-1}-L_jh_j+V_{j+1}H_{j+1}-V_jH_j+\Delta H-Q=0 \quad (5)$$

2.2. Mass Transfer in Gas Absorption

To size the absorber, the height is estimated in terms of the overall mass transfer coefficient. To account for the effect of chemical reactions on the mass transfer, the physical mass transfer coefficient of the liquid phase is adjusted by an enhancement factor that reflects the reaction kinetics. So, the gas-phase overall mass transfer coefficient is estimated as [3]:

$$\frac{1}{K_G}=\frac{1}{k_G}+\frac{Hn_{co2}}{k_LE} \quad (6)$$

The physical mass transfer coefficients of gas and liquid phases are estimated using empirical mass transfer correlations developed by Onda et al for randomly packed columns [4]. The following equations describe the correlations of interfacial area, gas-phase mass transfer coefficient, and liquid-phase mass transfer coefficient as a function of physical properties and flow velocity designs [4]:

$$\frac{\dot{a}}{\dot{a}_p}=1-\exp\left\{-1.45\left(\frac{\sigma_c}{\sigma_L}\right)^{0.75}\left(\frac{v_L}{\dot{a}_p\mu_L}\right)^{0.1}\left(\frac{v_L^2\dot{a}_p}{\rho_L^2 g}\right)^{-0.05}\left(\frac{v_L^2}{\rho_L\sigma_L\dot{a}_p}\right)^{0.2}\right\} \tag{7}$$

$$\frac{k_G RT}{\dot{a}_p D_G}=\epsilon\left(\frac{v_G}{\dot{a}_p\mu_G}\right)^{0.7}\left(\frac{\mu_G}{\rho_G D_G}\right)^{1/3}\left(\dot{a}_p d_p\right)^{-2} \tag{8}$$

where ϵ is 2 if $d_p < 0.012$ and 5.23 otherwise.

$$k_L\left(\frac{\rho_L}{\mu_L g}\right)^{1/3}=0.0051\left(\frac{v_L}{\dot{a}\mu_L}\right)^{2/3}\left(\frac{\mu_L}{\rho_L D_L}\right)^{-0.5}\left(\dot{a}_p d_p\right)^{0.4} \tag{9}$$

2.3. Equilibrium Flash for Solvent Regeneration

Assuming that no water is used to dilute the solvent and there are no vapor losses of the IL solvent in the capture process, a single-stage flash drum is employed for the stripping process, in which the vapor and liquid are assumed to be in equilibrium and steam required for the solvent regeneration is extracted from the plant steam cycle. The size of flash drum for solvent regeneration is determined in terms of empirical vapor velocity and liquid surge time designs. For chemical absorption, the energy requirements for solvent regeneration include the solvent heating and enthalpy of reaction plus heat of water vaporization if the water vapor is considered.

3. Engineering-Economic Model for Ionic Liquid-based CO_2 Capture

The performance model discussed above is linked to an engineering-economic model that estimate the capital cost, annual operating and maintenance (O&M) costs, and total annual levelized cost of electricity (LCOE) for the IL-based CCS system. This study employs the costing method and nomenclature of the Electric Power Research Institute's Technical Assessment Guide [5]. The total capital requirement of an IL-based capture system takes into account the direct costs plus a number of indirect costs such as the general facilities cost, engineering and home office fees, contingency costs, and owner's costs. As given in Table 1 for a post-combustion capture system, the major direct cost components include the direct contact cooler, flue gas blower, circulation pump, lean-solvent cooler, absorber and stripper, lean/rich solvent heat exchanger, steam extractor and reboiler, solvent processing unit, solvent reclaimer, as well as CO_2 product compression.

Table 2 summarizes major fixed and variable operating and maintenance (O&M) cost components. Fixed O&M costs include operating labor, maintenance costs, and administrative and support labor costs. Variable O&M costs include IL makeup, chemicals, solid waste treatment, power use, and CO_2 transport &storage.

Table 1 Capital cost components

CO_2 Capture Process Area Costs	**CO_2 Capture Plant Costs**
Direct contact cooler	Process facilities capital
Flue gas blower	General facilities capital
Absorber	Engineering. & home office fees
Heat Exchangers/coolers	Project contingency cost
Solvent pumps	Process contingency cost
Sorbent regenerator	Interest charges
Reboiler	Royalty fees
Steam extractor	Preproduction (startup) cost
Sorbent reclaimer	Inventory capital
Sorbent processing	
CO_2 product compression	
Process Facilities Capital (sum of above)	**Total Capital Requirement (sum of above)**

Table 2 Operating and maintenance cost components

Variable Cost Component	**Fixed Cost Component**
Solvent makeup	Operating labor
Chemicals	Maintenance labor
Reclaimer waste disposal	Maintenance material
Electricity	Admin. & support labor
CO_2 transport and storage	
Total Variable Cost (sum of above)	**Total O&M Cost (sum of above)**

4. Case Studies

The chemically tunable IL selected for this systems analysis is trihexyl-(tetradecyl)phosphonium 2-cyanopyrrolide ([P66614][2-CNpyr]) synthesized by researchers at the University of Notre Dame. This IL achieves a 1:1 and reversible chemical reaction between [2-CNpyr]− and CO_2, resulting in an efficient separation [1-2]. The typical absorption and stripping process is adopted for the IL-based carbon capture. The multi-stage equilibrium process model is used to simulate the adiabatic absorption process. In this case study the CO_2 of flue gas is assumed to be the only component transferred from the gas phase to liquid phase. A generalized Sherwood/Leva/Eckert correlation is adopted to estimate the gas-phase pressure drop across the absorber [6].

The technical and cost models are applied to evaluate the IL-based system for capturing CO_2 from the flue gas from a 650 MW (gross) supercritical pulverized coal power plant. Table 3 presents the assumptions of major technical and economic parameters. The direct capital costs of absorbers and strippers are scaled based on the vessel size from those reported in a recent system analysis on ILs for post-combustion CO_2 capture [7]. Table 4 summarizes the preliminary performance and cost model results for the IL-based system with 90% CO_2 capture. In this paper we report the metric of "cost of CO_2 captured" which is currently favored by the U.S. Department of Energy as the benchmark cost metric for an improved CO_2 capture system. This measure of cost is estimated as the total annualized cost divided by the amount of CO_2 captured. The preliminary case study results show that for 90% CO_2 capture, the cost of CO_2 capture for an IL-based capture system is about $62/tonne (in constant 2011 dollars). This is higher than the U.S. Department of Energy's target at $40 per metric ton of CO_2 captured for new generation

solvents [8], mainly due to a large capital cost. However, current process designs for the IL-based capture system are not yet optimized so these results remain preliminary.

Table 3 Major technical and economic assumptions

Performance Parameter	Unit	Value	Cost Parameter	Unit	Value
Plant capacity factor	%	75	Fixed charge factor	fraction	0.113
Flue gas flow rate	kmole/hr	94,980	Construction time	yr	3
Flue gas CO_2 concentration	mol. fraction	0.12	General facilities capital	% PFC	10
Number of trains	#	4	Engineering & overhead fees	% PFC	7
Flue gas temperature	^oC	40	Project contingency cost	% PFC	30
Lean solvent temperature into absorber	^oC	40	Process contingency cost	% PFC	30
Absorber operating pressure	bar	1.0	Misc. capital cost	%TPI	2
Number of equilibrium stages per vessel	#	5	Inventory capital	%TPC	0.5
CO_2 concentration in lean solvent	mol. fraction	0.050	Total maintenance cost	%TPC	2.5
Cold-side temperature approach for rich/lean heat exchanger	^oC	5	Labor fee	$/hr	34.65
Stripping temperature	^oC	160	Solvent makeup cost	$/t	10,000
CO_2 product pressure	bar	153			

Table 4 Preliminary performance and cost results for an IL-based system with 90% CO_2 capture

Parameter	Unit	Value
Performance Results CO_2 concentration in rich solvent stream	mol. fraction	0.19
Lean solvent flow rate per train	kmole/hr	15232
Pressure drop across absorber	kPa	12
Absorber height	m	45.5
Absorber diameter	m	11.1
Stripping pressure	bar	1.03
Stripper height	m	27.1
Stripper diameter	m	8.7
Steam use for solvent regeneration	kJ/kg CO_2	3627
Total equipment power use	MW	68.7
Cost Results Total capital requirement	2011M$	1121
Fixed O&M cost	2011M$/yr	29.3
Variable O&M cost	2011M$/yr	29.6
Total O&M cost[a]	2011M$/yr	58.9
Cost of CO_2 captured [a,b]	2011$/t	62.4

[a] This item does not include the CO_2 transport and storage costs.
[b] The cost of CO_2 captured in constant dollars is estimated as the total annualized cost divided by the total amount of CO_2 captured.

Figure 2 further presents the "cost of CO_2 captured" for a range of CO_2 removal efficiencies The minimum capture cost occurs at a removal rate of about 85% for CO_2, which implies that for partial CO_2 capture (e.g. 40-50%), a bypass design is cost-effective for an IL-based CCS system. Note that the cost of CO_2 captured may have a different behaviour that other widely-used cost metrics not shown here, such as the cost of CO_2 avoided (which includes CO_2 transport and storage costs plus the cost impact of additional CO_2 emissions associated with process energy requirements).

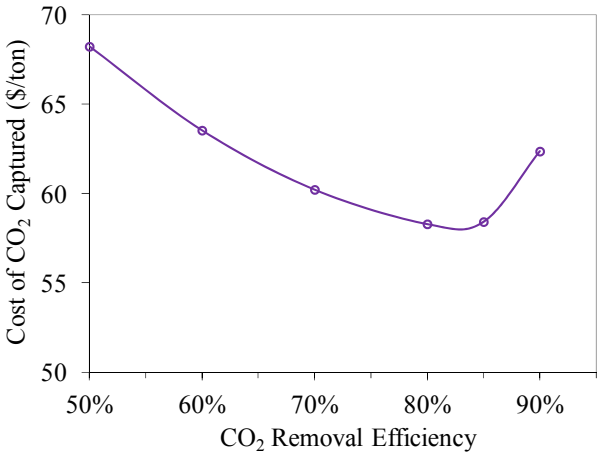

Fig. 2 Cost of CO_2 captured as a function of removal efficiency

5. Summary

The preliminary results of the case study presented here show that the most cost-effective "cost of CO_2 captured" was found to occur at a removal efficiency of about 85% for the IL studied. However, the overall cost of the IL-based capture system modeled was higher than the U.S. DOE's cost target for new generation technologies for post-combustion capture at a new coal-fired plant. Note that in the absence of additional data these results do not reflect the potential cost and performance impacts of other flue gas constituents such as sulfur and water vapor. However, current process designs for IL systems are not yet optimized and models and process designs will continue to be improved. Other important metrics for comparing the cost of plants employing different CCS systems, such as added LCOE for CCS and CO_2 avoidance cost, will be reported in future comparative cost assessments.

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